Theory and Parameter Free Calculations of EELS and X-ray Spectra

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There has been significant progress in both the theory and calculations of x-ray absorption (XAS), electron energy loss (EELS) and related spectroscopies [1,2]. These techniques are widely used to probe the properties of complex materials. Here we focus primarily on EELS, in which fast electrons are used as probe particles from modern scanning transmission electron microscopes (STEM). The advantage of EELS over XAS is its superior spatial and energy resolution, yielding measurements on a sub-Å atomic scale, with energy resolution now in the meV range. On the other hand, EELS is mostly limited to near-edge core-loss spectra (ELNES) within about 100 eV of an edge, or to the low-loss spectrum due to its rapidly decaying cross-section with energy. For similar reasons, the fine structure in EELS (EXELFS) is used less often than EXAFS. Both XAS, and EELS have been simulated with various levels of sophistication. A key goal of our work has been to develop theoretical methods that improve on approximate analysis techniques, e.g. comparisons of measured spectra with standards, model atomic calculations, or symmetry projected densities of states.

We begin with a summary of the theory together with a description of several methods now used for practical calculations. In particular we discuss the real-space Green's function (RSGF) approach used in the FEFF codes [1,2]. These codes are highly efficient computationally, and are applicable to periodic and aperiodic systems alike throughout the periodic table. A number of features have been incorporated in FEFF specifically for EELS calculations. For example, the code yields both relativistic and polarization dependent EELS, as well as self-consistent projected densities of states. Thus the approach can significantly improve on approximate methods, such as hydrogenic atomic models for EELS cross-sections. An important feature is the treatment of relativistic effects of the probe eslectrons, which can now have energies of order 300 keV or higher [3]. At relativistic energies the Coulomb interaction is compressed along the direction of propagation, leading to anisotropic polarization dependence. As a result the "magic angle" - the value of the collection angle at which the measurement's dependence on specimen orientation vanishes - is quite different from that predicted by non-relativistic codes. Finally the EELS module in FEFF also includes instrument effects such as the dependence on collection and convergence angles in order to facilitate interpretation of the spectra.

However, one of the limitations of the RSGF approach is a loss of accuracy near the edge or in the low-loss regime. Likewise, computational methods based on density functional theory (DFT) often lose accuracy due to strong excitonic effects on the spectra of many systems. To address these limitations, techniques based on the Bethe-Salpeter equation (BSE) have been developed for near-edge spectra (XANES) and near-edge EELS, and low loss spectra. These include the hybrid code OCEAN for core spectra [4], and AI2NBSE for low-energy spectra. These codes use the NIST BSE solver with Kohn-Sham wave functions as a basis from auxiliary electronic structure codes like ABINIT.

These methods still have other limitations. In particular, they often use simplified models to account for the many-body effects of inelastic losses and thermal vibrations. To address these effects, efforts have been made to develop improved theoretical methods that offer the prospect of parameter free

calculations of the dominant many-body effects. These methods are based on first principles calculations of the dielectric and vibrational response of a system. In particular calculations of the dielectric function over a broad spectrum can be carried out with the same codes, yielding system dependent self-energies and mean-free paths, as well as intrinsic losses due to multi electron excitations. Vibrational motion and disorder can be treated in terms of correlated Debye-Waller factors in FEFF. However, first principles calculations of the dynamical matrix can also yield vibrational damping in terms of multiple-scattering Debye–Waller factors [1,2]. While these effects have been difficult to include in the BSE, we show that they can be included approximately as an energy dependent loss term in the electron self-energy. The treatment of inelastic losses requires corrections to the quasi-particle approximation. For example, here we discuss how they can be included in terms of an energy-dependent spectral function derived from a quasi-boson model and cumulant-expansion techniques [5]. The theory can also be extended to include extrinsic losses and interference effects, and explains the cross-over from the adiabatic to sudden approximation. Remarkably the approach can also treat some strong correlation effects, e.g. charge-transfer satellites [6].

In summary, the development of new algorithms and *ab initio* methods for EELS and XAS calculations have led to improved, and broadly applicable x-ray and electron spectroscopy codes. As a result, one can now use a combination of codes to calculate EELS quantitatively over the full spectrum, from the UV-VIS to x-ray energies. These advances suggest the possibility of a virtual STEM, i.e. an automated workflow that combines several theoretical codes in order to simulate EELS and to facilitate the analysis of EELS data. To that end, we have developed a new Python-based workflow tool dubbed Corvus [7], which can facilitate multiple disparate calculations needed for this purpose. [8]

References:

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